PREPARATION AND CRYSTAL STRUCTURE OF A SELENOANTIMONATE $[\text{Fe}(\text{en})_3][\text{enH}]\text{SbSe}_4$

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Abstract

Low temperature synthesis has produced a new selenoantimonate, $[\text{Fe}(\text{en})_3][\text{enH}]\text{SbSe}_4$ (**I**). Crystals of **I** were grown at 160 °C in ethylenediamine solution. Compound **I** crystallizes in triclinic crystal system, space group *P*-1 (no. 2), with unit cell constants $a = 8.916(2)$ Å, $b = 9.679(2)$ Å, $c = 14.345(4)$ Å, $\alpha = 104.71(3)^\circ$, $\beta = 92.51(2)^\circ$, $\gamma = 110.14(2)^\circ$, $V = 1112.4(5)$ Å³ and $Z = 2$. Structural refinement using 2850 reflections ($F_o > 4(F_\sigma)$) and 204 variables resulted in 0.04 for R1 and 0.06 for wR2. **I** contains molecular Zintl anions $(\text{SbSe}_4)^{3-}$ and metal coordination complex $[\text{Fe}(\text{en})_3]^{2+}$ and $[\text{enH}]^+$ cations. The metal complex is present with 72% as *lel*₂*ob* conformer and 28% as *lel*₃ conformer.

1. Introduction

One of current interests in the synthesis of solid-state metal chalcogenides lies in the exploration of low temperature routes. The low temperature approach offers the advantage for the synthesis and ultimately designing of metastable materials, and provides the possibility for studying and understanding mechanisms involved in solid-state reactions [1]. Examples of low temperature techniques employed in the crystal growth of molecular tellurometalates and solid-state metal tellurides of extended structures include solvent extraction of intermetallic alloys [2], nonaqueous solution phase reactions [3], and electrochemical synthesis [4]. We have recently developed a new synthetic route which involves the use of ethylenediamine both as a reactant and as a solvent under solvothermal conditions [5]. The method has produced a number of new Zintl compounds containing molecular and extended anionic structures and transition metal coordination complex cations [6]. All of these compounds are obtained at relatively low temperatures (< 200 °C) and represent thermodynamically metastable phases. Here, we report the synthesis and crystal structure of $[\text{Fe}(\text{en})_3(\text{enH})]\text{SbSe}_4$, a new selenoantimonate prepared via solvothermal reactions at 160 °C.

2. Experimental Section

2.1 Chemicals.

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Antimony (III) chloride (99%, Alfa-AESAR), iron (II) chloride (99.5%, Alfa-AESAR), Se (99.5%, Alfa-AESAR), and Rb_2Se (Rb, 99.9+%, Strem Chemicals) were used as starting materials. Rb_2Se was prepared by a reaction using stoichiometric amounts of Rb and Se in liquid ammonia. Ethylenediamine (99%, anhydrous, Fisher Scientific) was used as solvent in all of the reactions.

2.2 Single Crystal Growth.

Dark brown, column-like crystals of compound **I** were isolated from a solvothermal reaction containing 0.0625 g (0.25 mmol) of Rb_2Se , 0.0570 g (0.25 mmol) of $SbCl_3$, 0.0317 g (0.25 mmol) of $FeCl_2$ and 0.0592 g (0.75 mmol) of Se. All of the starting materials were weighed and mixed in a glove box under inert argon atmosphere. The mixture was then transferred to a thick-wall Pyrex tube (9 mm OD, ca. 5 inches long) and approximately 5.5 mmol of the solvent, ethylenediamine (en), was added. After the sample was condensed by liquid nitrogen, the reaction tube was sealed under vacuum ($\sim 10^{-3}$ torr) and placed in an oven at $160^\circ C$ for 7 days before cooled to room temperature. The reaction product was then washed with 35% and 95% ethanol and dried with anhydrous diethyl ether. Microprobe analysis on the selected crystals of **I** using a JEOL JXA-8600 Superprobe gave the approximate composition of Fe:Sb:Se = 1:1:4.

2.3 Crystal Structure Determination.

A brown column shaped crystal (0.20 x 0.06 x 0.02 mm) of **I** was mounted on a glass fiber in air at room temperature on a Siemens SMART CCD area-detector diffractometer. Graphite-monochromatized Mo-K α radiation was used with the generator working at 50 kV and 35 mA. Cell parameters and the orientation matrix were obtained from the least-squares refinement on 176 reflections measured in three different sets of 15 frames each, in the range $3 < \theta < 25^\circ$ in the positive and negative range. Table I gives the unit cell parameters together with other details associated with data collection and refinement. The intensity data were collected using the ω -scan technique within the limits $4 < 2\theta < 54^\circ$ in the full sphere. Frame width was set at 0.3° and the detector exposition for each frame was 20 s. The sample-detector distance was fixed at 5.5 cm. The first 50 frames were recollected

Table I. Crystallographic Data for $[Fe(en)_3][enH]SbSe_4$ (**I**).

chemical formula	$C_8H_{33}N_8FeSbSe_4$	formula weight	734.86
crystal system	Triclinic	space group	$P-1$ (No.2)
a =	8.916(2) Å	$\alpha =$	$104.71(3)^\circ$
b =	9.679(2) Å	$\beta =$	$92.51(2)^\circ$
c =	14.345(4) Å	$\gamma =$	$110.14(2)^\circ$
V =	1112.4(5) Å ³	$\rho_{calc} =$	2.194 g cm ⁻³
Z =	2	$\mu =$	8.418 mm ⁻¹
T =	293(2) °K	$\lambda =$	0.71073 Å
R indices ^a [$F_o > 4\sigma(F_o)$] (2850 data)		R1 0.0403, wR2 0.0629	
R indices ^b (all data, 4213 reflections)		R1 0.0815, wR2 0.0727	

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR2 = [\sum (F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$$

$$\text{Weighting: } w = 1 / [\sigma^2(F_o^2) + (0.0950P)^2 + 16.1981P] \text{ where } P = (F_o^2 + 2F_c^2)/3$$

at the end of data collection to monitor the crystal decay, which was not observed, thus no time-decay correction was needed. The 1270 collected frames were then processed by software SAINT and an absorption correction (transmission range 0.602–0.825) was applied using the software SADABS on the 9134 collected reflections (4213 of which are unique, with $R(\text{int}) = 0.0442$). The structure was solved by direct methods with SIR92 [7] and refined with full-matrix least squares method on F_o^2 using all the independent reflections. One carbon atom was statistically disordered on two different position and the occupation was refined to the values of C(12A) 0.72(2) and C12B 0.28(2). All of the nitrogen atoms occupy two crystallographically different positions. Anisotropic thermal displacements were assigned to all non-hydrogen atoms, but for C(12B) due to the small occupancy. Hydrogens were set at fixed distances and angles from their related carbon atoms and not refined. All calculations were performed using SHELX-93 [8]. Crystal drawings were produced with SCHAKAL [9]. Final atomic coordinates, average temperature factors, selected bond lengths and angles for **I** are listed in Tables II–III.

3. Results and Discussion

The crystal structure of **I** contains tetrahedral $(\text{SbSe}_4)^{3-}$ anions, and $[\text{Fe}(\text{en})_3]^{2+}$ and $(\text{enH})^+$ cations (see Figure 1). The Sb–Se bond distances range from 2.468(1) to 2.482(1) Å, which are comparable with those found in other related compounds containing $(\text{SbSe}_4)^{3-}$ anions, 2.438–2.50 Å [10–11]. The monoprotonated ethylenediamine cations have been reported previously in several cases, including both

Table II. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^3$) for $[\text{Fe}(\text{en})_3][\text{enH}]\text{SbSe}_4$ (**I**). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$	s.o.f.
Sb	-0.11812(5)	0.07543(5)	0.22817(3)	0.02376(13)	1
Se(1)	-0.10849(8)	0.18604(8)	0.09030(5)	0.0321(2)	1
Se(2)	0.16382(8)	0.16463(8)	0.30814(5)	0.0344(2)	1
Se(3)	-0.28580(9)	0.17787(9)	0.33763(6)	0.0420(2)	1
Se(4)	-0.23560(9)	-0.20898(8)	0.16484(5)	0.0355(2)	1
Fe	0.21191(11)	-0.31209(10)	0.31620(7)	0.0259(2)	1
N(11)	0.1893(9)	-0.2125(8)	0.1970(5)	0.059(2)	1
C(12A)	0.144(2)	-0.352(2)	0.1034(8)	0.056(5)	0.72(2)
C(12B)	0.286(4)	-0.255(3)	0.123(2)	0.038(9)	0.28(2)
C(13)	0.2414(11)	-0.4357(9)	0.1076(6)	0.054(2)	1
N(14)	0.2336(6)	-0.4880(6)	0.1930(4)	0.0335(14)	1
N(21)	0.1522(6)	-0.1404(6)	0.4251(4)	0.0308(14)	1
C(22)	-0.0264(8)	-0.1920(8)	0.4258(5)	0.038(2)	1
C(23)	-0.0967(8)	-0.3638(8)	0.3994(6)	0.043(2)	1
N(24)	-0.0521(6)	-0.4296(6)	0.3069(4)	0.040(2)	1
N(31)	0.4768(6)	-0.1917(6)	0.3492(4)	0.041(2)	1
C(32)	0.5290(8)	-0.2108(9)	0.4416(6)	0.048(2)	1
C(33)	0.4484(9)	-0.3739(9)	0.4438(6)	0.048(2)	1
N(34)	0.2722(7)	-0.4186(6)	0.4248(4)	0.041(2)	1
N(41)	-0.7296(6)	0.1544(6)	0.0719(4)	0.039(2)	1
C(42)	-0.5571(8)	0.1791(9)	0.0723(6)	0.049(2)	1
C(43)	-0.4521(8)	0.3464(8)	0.1043(6)	0.042(2)	1
N(44)	-0.4642(6)	0.4189(7)	0.2034(4)	0.047(2)	1

Table III. Selected Bond Lengths [Å] and angles [deg] for $[\text{Fe}(\text{en})_3][\text{enH}]\text{SbSe}_4$ (I).

Sb-Se(1)	2.4682(10)	Sb-Se(2)	2.4760(11)	Sb-Se(3)	2.4737(10)
Sb-Se(4)	2.4822(11)	Fe-N(14)	2.188(5)	Fe-N(11)	2.198(6)
Fe-N(21)	2.202(5)	Fe-N(24)	2.214(5)	Fe-N(31)	2.211(5)
Fe-N(34)	2.215(5)	C-N ave.	1.473(8)	C-C ave	1.527(8)
Se(1)-Sb-Se(3)	106.31(3)	Se(1)-Sb-Se(2)	106.60 (3)		
Se(3)-Sb-Se(2)	111.51(4)	Se(1)-Sb-Se(4)	109.01(4)		
Se(3)-Sb-Se(4)	112.10(4)	Se(2)-Sb-Se(4)	111.02(4)		

chalcogenides and selenoantimonates [10, 12-13]. The proton was included in the structure to balance the charge. Formal oxidation state assignment therefore suggests a Sb(V), Se(-II) and Fe(II). The average Fe-N distance of 2.21 Å agrees well with high spin Fe(II) amine complexes [14] and is very similar to those reported earlier by us [5]. The cation $[\text{Fe}(\text{en})_3]^{2+}$ is present in two conformers, 72% as lel_2ob and 28% as lel_3 from refined occupancy of the disordered C(12A) and C(12B) (see Section 2.3). In the isostructural $[\text{Ge}(\text{en})_3][\text{enH}]\text{SbSe}_4$ [10], such disorder is not evident, probably due to the imperfection of the crystal (final R1 10%).

Compared to the preparation of $[\text{Ge}(\text{en})_3][\text{enH}]\text{SbSe}_4$ [10], single crystals of **I** were grown by a relatively easier and simpler route. Our solvothermal reactions also yielded suitably sized and good quality crystals whose structure determination was carried out at room temperature.

Figure 1. Crystal structure of $[\text{Fe}(\text{en})_3][\text{enH}]\text{SbSe}_4$. The shaded circles are Sb, large solid circles, Se and large open circles, Fe. The medium sized solid and open circles are N and C, respectively.

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